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PAPERS READ BEFORE THE ACADEMY.

I.

RESEARCHES ON THE HEXATOMIC COMPOUNDS OF COBALT.*

BY WOLCOTT GIBBS, M.D.

Presented, Oct. 13, 1874.

IN the joint memoir of Genth and myself on the ammonia-cobalt bases it was stated that xanthocobalt is not the only product of the action of nitrous acid gas upon ammoniacal solutions of cobalt. A further investigation of this and other related subjects was then promised. I propose now to resume the study of this class of compounds from the standpoint of the chemistry of the present day. The progress of science has rendered necessary the abandonment of my former theoretical views, as well as the adoption of the new notation. It has also, as I shall endeavor to show, lent a peculiar interest to the study of the ammonia-metallic bases.

In studying the action of the alkaline nitrites upon salts of cobalt, or upon those of the different series of ammonia-cobalt compounds, a principal difficulty arises from the varying nature and relative proportions of the products obtained under various conditions of temperature, concentration of solutions employed, and duration of action. I have endeavored to cover the whole ground as completely as possible.

1. *Action of Ammonia and Ammonic Nitrite upon a Solution of Cobaltic Chloride and Ammonic Nitrate.* — When a warm solution of

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* Being Part II. of Researches on the Ammonia-cobalt Bases, by Wolcott Gibbs and F. A. Genth.

cobaltic chloride, $CoCl_2$, is mixed with ammonic nitrate, and then with a solution of ammonic nitrite, containing much free ammonia, the solution soon becomes deep orange, and after twenty-four hours deposits orange-brown crystals in large quantity. The mother liquor of these crystals is olive-green. By re-solution in hot water containing a few drops of acetic acid, and filtration, beautiful orange-yellow needles may be obtained as this filtrate cools. The crystals are perfectly free from chlorine, and represent the nitrate of a new series of ammonia-cobalt salts, the formula of the salts being

$$Co_2(NH_3)_8(NO_2)_4(NO_3)_2.$$

The formation of this salt is accompanied by an absorption of oxygen from the air, and may be expressed by the equation: —

$$2CoCl_2 + 2NH_4.NO_3 + 8NH_3 + 4NH_4.NO_2 + O = \\ Co_2(NH_3)_8(NO_2)_4(NO_3)_2 + 4NH_4Cl + 2(NH_4)_2O.$$

2. *Action of a Mixture of Ammonia and Potassic Nitrite upon Cobaltic Sulphate.* — When cobaltic sulphate is dissolved in water and a mixture of ammonia and potassic nitrite is added, the liquid speedily becomes brown upon the surface, and after a few hours orange-yellow crystals form upon the bottom and sides of the containing vessel, while a green flocky matter is at the same time deposited. When large quantities of material are operated upon, the complete oxidation requires several days. On filtering, a bright green mass mixed with orange-yellow crystals remains upon the filter: the filtrate is olive-green, and after standing often deposits small, brilliant orange-yellow scales. If the mass on the filter is treated with hot very dilute sulphuric acid, it instantly becomes bright orange, and by boiling dissolves. The filtered solution then deposits, on cooling, a splendid salt, which has the formula

$$Co_2(NH_3)_8(NO_2)_4SO_4,$$

and which is the sulphate corresponding to the nitrate already mentioned.

3. *Action of a Mixture of Ammonia and Potassic Nitrite upon Cobaltic Nitrate.* — When cobaltic nitrate is dissolved in water and a mixture of ammonia and potassic nitrite is added, the liquid speedily becomes brownish-orange, and after an hour begins to deposit bright orange-yellow crystals, mixed with a green flocky matter, precisely as in the case of the sulphate. By dissolving the orange-yellow crystals in boiling water, a few drops of acetic acid being added to prevent decomposition, a fine sherry-wine-colored solution is obtained, which, on cooling, deposits crystals of two different forms, the larger portion being in octahedrons, the smaller in prismatic forms. By careful mechanical

separation and recrystallization, these crystals may be separated and the two salts obtained pure for analysis. In this manner I found the octahedral salt to be nitrate of xanthocobalt, while the prismatic crystals are the nitrate of the octamin series above mentioned. In one experiment, of the octahedral salt,

0·3833 gr. gave 0·1890 gr. $CoSO_4 =$ 18·77 per cent cobalt.

The formula of nitrate of xanthocobalt, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4$, requires 18·73 per cent. Of the prismatic salt,

0·7369 gr. gave 0·4050 gr. $CoSo_4 =$ 20·92 per cent cobalt.

The formula of the nitrate of the new series,

$Co_2(NH_3)_8(NO_2)_4(NO_3)_2$, requires 20·99 per cent.

For greater certainty I made also a nitrogen determination in this nitrate: —

0·5668 gr. gave 168·5 c.c. nitrogen at 13·5° C. and $756{\cdot}1^{mm} =$ 34·79 per cent nitrogen.

The formula cited requires 34·88 per cent. The two salts were further readily recognized by their characteristic reactions. In my experiments the proportion of xanthocobalt salt formed was much the greater. The formation of the new nitrate may in this case be represented by the equation: —

$$2Co(NO_3)_2 + 8NH_3 + 4KNO_2 + OH_2 + O = Co_2(NH_3)_8(NO_2)_4(NO_3)_2 + 2KNO_3 + 2OKH;$$

and the formation of the nitrate of xanthocobalt by the equation: —

$$2Co(NO_3)_2 + 10NH_3 + 2KNO_2 + OH_2 + O = Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 + 2OKH.$$

The green flocky matter which accompanies the formation of the above-mentioned nitrates and sulphate is cobaltic hydrate, $Co(OH)_2 + 2OH_2$, and is of course due to the action of the potassic hydrate upon the solution of cobalt in excess. I varied the above process by adding ammonia first to the solution of cobaltic nitrate, and afterward the solution of potassic nitrite, but the results were the same.

4. *Action of Ammonia and Potassic Nitrite upon a Mixture of Cobaltic and Ammonic Sulphates.* — In this case as in the others the solution becomes brown and deposits an orange crystalline mass. If the mass is dissolved in water and a solution of potassic bromide is added, after standing, fine crystals are formed, which, after a single recrystallization, are pure bromide of xanthocobalt. In one experiment: —

0·5634 gr. gave 0·2496 gr. $CoSO_4 =$ 16·87 per cent cobalt.
0·7294 gr. gave 0·4496 gr. silver = 45·65 per cent bromine.

The formula, $Co_2(NH_3)_{10}(NO_2)_2Br_4$, requires cobalt 16·86, bromine 45·71. I did not succeed in finding the sulphate of the octamin series among the products in the single experiment which I made with the above-mentioned mixture. If present at all, its relative quantity must have been small. The formation of sulphate of xanthocobalt is easily explained by the equation: —

$$2CoSO_4 + 10NH_3 + 2KNO_2 + OH_2 + O = \\ Co_2(NH_3)_{10}(NO_2)_2(SO_4)_2 + 2OKH;$$

but it is not easy to see why the presence of ammonic sulphate should determine the production of sulphate of xanthocobalt in place of the sulphate of the octamin series.

With these preliminaries I pass to the description of the salts of the new octamin series. These salts as a class greatly resemble those of xanthocobalt, but are rather more stable. They have a fine sherry-wine color, are usually comparatively insoluble in cold, and are dissolved with difficulty even by boiling water. The solutions when neutral are decomposed by boiling, ammonia being evolved and a black powder precipitated. The addition of a small quantity of acetic acid serves to prevent the decomposition in hot solutions. Mineral acids, even in small quantity, usually produce more or less decomposition on heating. The salts crystallize with remarkable facility, resembling in this respect the salts of luteocobalt, which are, however, much more soluble. As the octamin salts are easily prepared in quantity, they may hereafter be found to possess some value as means of investigation from their remarkable power of crystallization.

Sulphate. — Of all the salts of this series the sulphate is that which is most easily prepared in quantity and free from other products. The general method of preparation has been already pointed out. The mixture of cobaltic hydrate and crude sulphate is to be boiled with very dilute sulphuric acid, filtered, and the solution allowed to stand for a few hours, when the sulphate separates almost completely, in consequence of its insolubility in cold water. The mother liquor contains a large quantity of cobaltic sulphate, and traces of the new salt together with potassic and ammonic sulphates. A second crystallization gives a perfectly pure salt. In large crystals the salt has a dark wine-red color, like the salts of xanthocobalt. It usually separates from hot concentrated solutions in small, very brilliant yellow scales, which, under the microscope, appear to belong to the quadratic system. The sulphate is remarkable for its insolubility. Cold water dissolves a very small quantity, the solution taking a golden-yellow color. Even in boiling water the salt is but slightly soluble; but dilute sulphuric acid dissolves it more readily and without decomposition, if the boiling be not continued too long. Stronger acid readily decomposes the sulphate by boiling. When boiled for some time with dilute chlorhydric acid, the solution gradually becomes violet-red, and on cooling deposits crystals of chloride of purpureocobalt. Of these crystals,

0·2825 gr. gave 0·1749 gr. $CoSO_4 = 23·56$ per cent cobalt.

The formula $Co_2(NH_3)_{10}Cl_6$ requires 23·55 per cent.

The decomposition is accompanied by effervescence from the escape of gas, apparently nitrogen mixed with a smaller quantity of nitrous acid vapors, and may perhaps be expressed by the equation: —

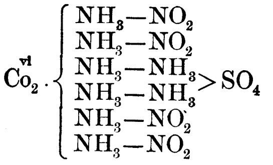
$$2Co_2(NH_3)_8(NO_2)_4SO_4 + 6HCl = Co_2(NH_3)_{10}Cl_6 + 2CoSO_4 + 12OH_2 + 2NO_2 + 12N.$$

In this reaction we pass from a lower to a higher ammonia-base, and Genth and I have shown that we may also pass from purpureocobalt to luteocobalt, or from the decamin to the dodecamin series, the higher term being in each case the product of the decomposition of the lower The formula of the sulphate in the new series is, as stated, $Co_2(NH_3)_8(NO_2)_4SO_4$. The following are the direct results of analysis: —

0·6142 gr. gave 0·3596 gr. $CoSO_4 = 22·28$ per cent cobalt.
0·4207 gr. gave 0·2454 gr. „ $= 22·21$ „ „
1·5547 gr. gave 0·6785 gr. $BaSo_4 = 17·98$ „ SO_4
0·6960 gr. gave 0·2903 gr. water $= 4·63$ „ hydrogen.
0·4693 gr. gave 123·5 c.c. nitrogen at 9·5° C. and $754·5^{mm} = 31·33$ per cent.

			Calculated.	Found.	
Cobalt	2	118	22·09	22·28	22·21
SO_4	1	96	17·97	17·98	
Hydrogen	24	24	4·49	4·63	
Nitrogen	12	168	31·46	31·33	
Oxygen	8	128	23·99		
		534	100·00		

On Blomstrand's view of the constitution of the ammonia-metallic bases, the formula of the sulphate may be written: —



$$\overset{vi}{Co_2}\cdot\left\{\begin{array}{l} NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NH_3 \\ NH_3-NH_3 \\ NH_3-NO_2 \\ NH_3-NO_2 \end{array}\right. \quad \begin{array}{l} NH_3-NH_3 \\ NH_3-NH_3 \end{array} > SO_4$$

I shall discuss this view more fully at the close of this paper.

Chloride. — The chloride of this series cannot be readily obtained by the action of a mixture of ammonia and potassic nitrite upon cobaltic chloride, since, as I shall show hereafter, other products are formed under these circumstances in much the larger quantities, salts of xanthocobalt predominating. It may, however, be easily prepared in quantity by boiling the crude sulphate with baric chloride and a very small quantity of chlorhydric acid. To avoid loss, the baric sulphate must be repeatedly and carefully washed with boiling water and a trace of free acid. The chloride then crystallizes from the filtrate in beautiful iridescent crystals. The forms of these crystals, together with those of other salts of this series, I hope hereafter to be able to give in detail. The chloride has the characteristic sherry-wine color of the salts of this series, and the small crystals are very brilliant and exhibit a remarkable iridescence.

The chloride is more soluble than the sulphate, but still belongs to the class of slightly soluble salts, and crystallizes almost completely from hot solutions as these become cold. The salt possesses in a high degree the sharply defined crystalline character of the members of this series, and forms a large number of compounds with metallic chlorides, many of which are of great beauty. The constitution of the chloride is represented by the formula

$$Co_2(NH_3)_8(NO_2)_4Cl_2,$$

as the following analyses show : —

0·5164 gr. gave 0.3152 gr. $CoSO_4 = 23{\cdot}24$ per cent cobalt.
0·6048 gr. gave 0·3683 gr. $CoSO_4 = 23{\cdot}18$ „ „
0·7188 gr. gave 0·3027 gr. silver = 13·84 „ chlorine.
0·4846 gr. gave 0·2152 gr. water = 4·92 „ hydrogen.
0·6160 gr. gave 172·5 c.c. nitrogen at 16° C. and $768{\cdot}2^{mm}$ = 32·91 per cent.

			Calculated.	Found.
Cobalt	2	118	23·18	23·18 23.24
Chlorine	2	71	13·94	13·84
Hydrogen	24	24	4·71	4·90
Nitrogen	12	168	33·00	32·91
Oxygen	8	128	25·17	
		509	100·00	

The corresponding bromide, $Co_2(NH_3)_8(NO_2)_4Br_2$, resembles the chloride so closely that no special description is necessary. In this salt,

0·3944 gr. gave 0·2059 gr. $CoSO_4 = 19{\cdot}87$.

The formula requires 19·73 per cent.

Hyperiodide. — When a solution of iodine in potassic iodide is added to one of the nitrate of this series, a magnificent crystalline cinnabar-red compound is precipitated, which may be washed with cold water, and afterward with a little alcohol, without decomposition. For analysis, the salt was dried in pleno over sulphuric acid. The crystals are small scales of unusual beauty and richness of color. They are slightly soluble in cold water, and are partially decomposed by boiling water with evolution of iodine vapors. Even long boiling, however, does not appear to decompose them completely. When heated with a solution of sodic sulphite, the salt instantly becomes yellow and is converted into the normal iodide. No similar compound is formed when a solution of potassic hyperiodide is added to one of nitrate of xanthocobalt. The formation of the hyperiodide may be represented by the equation:

$$Co_2(NH_3)_8(NO_2)_4(NO_3)_2 + 2KI_3 = Co_2(NH_3)_8(NO_2)_4I_6 + 2KNO_3.$$

In this salt,

0·5748 gr. gave 0·1494 gr. $CoSO_4 = 9{\cdot}87$ per cent cobalt.
0·4705 gr. gave 0·2550 gr. silver = 63·70 „ iodine.
0·3942 gr. gave 49 c.c. nitrogen at 14·5° C. and 736·8^{mm} = 14·10 per cent nitrogen.

			Calculated.	Found.
Cobalt	2	118	9·83	9·87
Iodine	6	762	63·50	63·70
Nitrogen	12	168	14·00	14·10
Hydrogen	24	24	2·00	
Oxygen	8	128	10·67	
		1200	100·00	

If we consider NO_2 as in part triatomic in this salt, the constitutional formula may be most simply represented by the expression: —

$$\overset{vi}{Co_2}\left\{\begin{array}{l} NH_3 - NO_2 \\ NH_3 - NO_2 = I_2 \\ NH_3 - NH_3 - I \\ NH_3 - NH_3 - I \\ NH_3 - NO_2 = I_2 \\ NH_3 - NO_2 \end{array}\right.$$

Nitrate. — I have already stated that the nitrate of this series may be formed by the action of a mixture of ammonia and ammonic nitrate upon a solution of cobaltic chloride and ammonic nitrate. It is much more convenient, however, to prepare it from the crude sulphate by double decomposition with baric nitrate. The sulphate is to be boiled with a small excess of baric nitrate and a little acetic acid, and the baric sulphate carefully washed to avoid loss of nitrate. From the filtered solution the new salt crystallizes almost completely, on cooling, in beautiful orange-yellow needles, and sometimes in distinct prismatic forms. It is much more soluble than the sulphate, though cold water takes up but little. Boiling water and dilute acid solutions dissolve it more readily. The reactions of the base may be studied most conveniently with this salt. The formula of the nitrate is

$$Co_2(NH_3)_8(NO_2)_4(NO_3)_2,$$

as the following analyses show: —

0·2405 gr. gave 0·1333 gr. $CoSO_4 = 21{\cdot}10$ per cent cobalt.
0·6564 gr. gave 0·2484 gr. water $= 4{\cdot}21$ per cent hydrogen.
0·6148 gr. gave 173·5 c.c. nitrogen at 4·5° C., and $762{\cdot}2^{mm} = 34{\cdot}83$ per cent.

			Calculated.	Found.
Cobalt	2	118	20·99	21·10
Hydrogen	24	24	4·27	4·21
Nitrogen	14	196	34·88	34·83
Oxygen	14	224	39·86	
		562	100.00	

The nitrate explodes, though not very violently, on being heated. Its solution gives with potassic ferrocyanide no precipitate at first, but after some hours beautiful garnet-red acicular crystals are formed. It is most easily distinguished from the nitrate of xanthocobalt by its crystalline form and by the extremely characteristic precipitates which its solution yields with potassic hyperiodide and with potassic chromate.

Chromate. — When a solution of potassic chromate is added to one of the nitrate of the octamin series, a most beautiful lemon-yellow salt is formed, which separates almost immediately in very brilliant scales which appear to belong to the quadratic system, and to be isomorphous with the sulphate. The salt is but slightly soluble in water. Its marked crystalline form renders it valuable in distinguishing the salts of this series from those of xanthocobalt. In this salt,

0·4660 gr. gave 0·2128 gr. $BaCrO_4 = 20{\cdot}95$ per cent CrO_4.
0·4659 gr. gave 119·5 c.c. nitrogen at 9·75° C. and $753{\cdot}5^{mm} = 30{\cdot}42$ per cent.

The formula, $Co_2(NH_3)_8(NO_4)_4CrO_4$, requires 20·97 per cent CrO_4 and 30·42 per cent of nitrogen.

Dichromate. — This salt is easily formed by adding a solution of potassic dichromate to one of the octamin nitrate. It separates after a few minutes in beautiful orange-yellow needles, which may be redissolved and again crystallized without decomposition. In appearance and solubility it can hardly be distinguished from the corresponding salt of xanthocobalt,

$$Co_2(NH_3)_{10}(NO_2)_2(Cr_2O_7)_2.$$

The formula of this salt is: —

$$Co_2(NH_3)_8(NO_2)_4Cr_2O_7.$$

0·5604 gr. gave 0·4315 gr. $BaCrO_4 = 32·91$ per cent Cr_2O_7.

The formula requires 33·06 per cent. The determination of CrO_4 and Cr_2O_7, in this and similar compounds containing NO_2, can be effected more accurately by means of a baric salt than by mercurous nitrate, since the nitrous compound always reduces a little chromic acid to chromic sesquioxide.

Platino-chloride. — A solution of sodic platino-chloride, $PtCl_6Na_2$, produces in one of the new nitrate after a time fine orange-brown prismatic crystals, which, however, cannot easily be recrystallized without decomposition. The crystals were washed with cold water, dried by pressure, and then over sulphuric acid. The analysis was made by boiling the salt with zinc and dilute sulphuric acid, filtering off and weighing the reduced platinum and determining the chlorine in the filtrate by silver. In another portion of the salt the platinum and cobalt were determined together by gentle ignition in a current of hydrogen gas. In this manner,

0·3959 gr. gave 0·0921 gr. platinum and 0·3016 gr. silver = 23·26 per cent platinum and 25·04 per cent chlorine.

0·4459 gr. gave 0·1652 gr. platinum and cobalt = 37·04 per cent. Subtracting 23·26 per cent platinum from this, we have 13·78 per cent cobalt.

		Calculated.	Found.
Cobalt	2	13·91	13·78
Chlorine	6	25·12	25·04
Platinum	1	23·23	23·26

The formula of this salt is therefore:—

$$Co_2(NH_3)_8(NO_2)_4Cl_2 + PtCl_4.$$

Auro-chloride. — A solution of auro-chloride of sodium, $AuCl_4Na$, produces immediately in one of the octamin nitrate a beautiful crystalline precipitate, with a fine canary-yellow color and silky lustre. Small quantities of this salt may be dissolved in boiling water without decomposition, but it is very difficult to recrystallize it without great loss from the reduction of the gold. When boiled for a short time the salt is almost completely decomposed. It is remarkably insoluble in cold water. For analysis the salt was dried on bibulous paper, and afterward in pleno over sulphuric acid. The analysis was effected by boiling the salt with zinc as in the case of the platinum salt, and determining the chlorine in the filtrate by silver, but the gold precipitated was found to contain much metallic cobalt. Another analysis was made by simply heating with sulphuric acid, precisely as in the process which Genth and myself introduced for the determination of cobalt in these salts, and then washing and weighing the gold. This method was found to give excellent results. In this manner,

0·4791 gr. gave 0·3697 gr. silver = 25·36 per cent chlorine.

0·3942 gr. gave 0·2483 gr. Au + $CoSO_4$ and 0·1391 gr. gold, and by difference 0·1092 gr. $CoSO_4$ = 10·54 per cent cobalt and 35·30 per cent gold.

		Calculated.	Found.
Cobalt	2	10·57	10·54
Gold	2	35·30	35·30
Chlorine	8	25·44	25·36

The formula of the salt is therefore: —

$$Co_2(NH_3)_8(NO_2)_4Cl_2 + 2AuCl_3.$$

Erdmann's Salt. — O. L. Erdmann,* in 1866, described a remarkable salt which is formed when a solution of potassic nitrite is added to a solution of cobaltic chloride containing an excess of ammonic chloride. The liquid quickly assumes a dark orange color, becomes strongly acid and evolves red vapors. After a time very beautiful oblique rhombic crystals are deposited, which, according to Erdmann, have the formula (old style)

$$Co_2O_32NH_3,\ 3NO_3 + KO,NO_3.$$

In modern notation the formula of Erdmann's salt may be written: —

$$Co_2(NH_3)_4(NO_2)_8K_2.$$

Erdmann states that the potassium in this salt may be replaced by other metals, and describes the corresponding ammonium and silver salts. These compounds are especially interesting because they hold an intermediate position between the two series represented respectively by the terms

$$Co_2(NH_3)_{12}Cl_6 \text{ and } Co_2(NO_2)_{12}K_6.$$

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* Journal für prakt. Chemie, xcvii. 385.

I propose therefore to speak of them more in detail hereafter, and to confine myself at present to their relations to the salts of the octamin series.

When a solution of Erdmann's salt, $Co_2(NH_3)_4(NO_2)_8K_2$, is added to one of the octamin nitrate, a beautiful crystalline precipitate is formed, which after washing with cold water may be redissolved in hot water and then separates in fine orange-yellow granular crystals. The equation representing the reaction is here

$$Co_2(NH_3)_8(NO_2)_4(NO_3)_2 + Co_2(NH_3)_4(NO_2)_8K_2 = 2KNO_3 + \\ \{Co_2(NH_3)_4(NO_2)_8\}''\{(Co_2(NH_3)_8(NO_2)_4\}''.$$

The new salt gives with reagents the reactions of the salts of the octamin series. The relation between the two complex atoms which form a molecule of the new salt is worthy of notice, the number of atoms of ammonia and nitroxyl in the one corresponding to the number of atoms of nitroxyl, NO_2, and of ammonia in the other; one complex atom being, to use Graham's convenient expression, chlorous and the other zincous. We have furthermore the relation expressed by the equation: —

$$\{Co_2(NH_3)_4(NO_2)_8\}\{(Co_2(NH_3)_8(NO_2)_4\} = 2Co_2(NH_3)_6(NO_2)_6.$$

Now I shall show, farther on, that there exist several other salts, the empirical constitutions of which may be represented also by multiples of the formula

$$Co_2(NH_3)_6(NO_2)_6,$$

so that we have here, for the first time, I believe, in inorganic chemistry, a series of strictly metameric bodies. In the salt of the octamin series,

$$0{\cdot}2600 \text{ gr. gave } 0{\cdot}1622 \text{ gr. } CoSO_4 = 23{\cdot}74 \text{ per cent cobalt.}$$

The formula requires 23·79 per cent.

The salts which I have described are not the only ones which contain 8 atoms of ammonia with 2 atoms of cobalt. In our memoir Genth and I made mention of a leek-green crystalline body which we obtained in more than one reaction in quantities too small for analysis, and which we termed, provisionally, Praseocobalt. Braun subsequently denied the existence of any such substance; but, in an excellent paper on the ammonia-cobalt compounds, F. Rose has not merely described and analyzed the body in question, but has given a method of preparing it in quantity. Rose gives for the formula of this salt Co_2Cl_3 N_4H_{12} (old style). I should write this

$$Co_2(NH_3)_8Cl_6,$$

and give it the atomistic formula

$$Co_2 \left\{ \begin{array}{l} NH_3-Cl \\ NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-NH_3-Cl \\ NH_3-Cl \\ NH_3-Cl \end{array} \right.$$

It thus forms the type of a special octamin series, the relations of which to the salts which I have described are easily seen by comparing the formulas which I have given. Rose has not described any other salts of this series. It seems possible that my series may be derived from this by acting upon the chloride with argentic nitrite: we may have

$$Co_2(NH_3)_8Cl_6 + 4AgNO_2 = Co_2(NH_3)_8(NO_2)_4Cl_2 + 4AgCl,$$

but I have as yet made no experiments in this direction. Finally Künzel * described, many years since, a hyposulphate, to which he gave the formula $Co_2O_3 + 4NH_3 + 2S_2O_5$ (old style). This formula becomes, in my view, $Co_2(NH_3)_8S_4O_{13}$, and the salt then belongs to the octamin series; but it is possible that its empirical constitution has not yet been correctly given.

In treating of the salts of my new series, it appeared to me more in accordance with the theoretical views which I have adopted to abstain from trivial names. All the members of this series may however be regarded as containing the complex atom $Co_2(NH_3)_8(NO_2)_4$, which alone is constant and which from one point of view may be regarded as a diatomic radical or residue, and those who justify the use of trivial names by their convenience may find the name " Croceocobalt " expressive and appropriate.

5. The salts described by Fremy † under the names of chloride, nitrate, and sulphate of Fuscocobalt contain also eight atoms of ammonia, and may be regarded as belonging to the octamin series. These salts have, according to Fremy, respectively the formulas: —

$$Co_2(NH_3)_8 . O . Cl_4 + 3OH_2,$$
$$Co_2(NH_3)_8 . O . (NO_3)_4 + 3OH_2,$$
$$Co_2(NH_3)_8 . O . (SO_4)_2 + 4OH_2,$$

in modern notation. They are brown resinous masses, are difficult to obtain in a state of purity, and have as yet been but little studied. If

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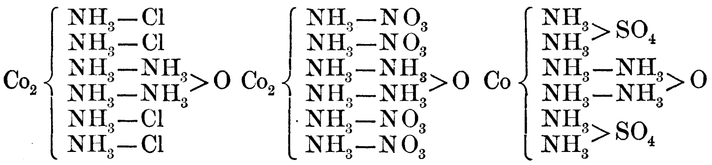
* Journal für prakt. Chemie, lxxii. 218.

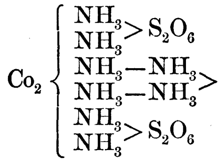
† Ann. de Chimie et de Physique [3], tome xxxv. p. 257.

we admit that the formulas are accurate, we may write them, in accordance with the theoretic views which I have adopted, as follows:* —



$$Co_2\left\{\begin{array}{l} NH_3-Cl\\ NH_3-Cl\\ \begin{array}{l}NH_3-NH_3\\ NH_3-NH_3\end{array}\!\!>O\\ NH_3-Cl\\ NH_3-Cl\end{array}\right. \quad Co_2\left\{\begin{array}{l} NH_3-NO_3\\ NH_3-NO_3\\ \begin{array}{l}NH_3-NH_3\\ NH_3-NH_3\end{array}\!\!>O\\ NH_3-NO_3\\ NH_3-NO_3\end{array}\right. \quad Co\left\{\begin{array}{l} \begin{array}{l}NH_3\\ NH_3\end{array}\!\!>SO_4\\ \begin{array}{l}NH_3-NH_3\\ NH_3-NH_3\end{array}\!\!>O\\ \begin{array}{l}NH_3\\ NH_3\end{array}\!\!>SO_4\end{array}\right.$$

Jörgensen † suggests that these salts may contain hydroxyl in place of oxygen. There is at present no method of deciding the question, and I have adopted the view which seems to me the most probable. Künzel's hyposulphate above mentioned may be regarded as belonging to this series, and as having the structural formula: —



$$Co_2\left\{\begin{array}{l} \begin{array}{l}NH_3\\ NH_3\end{array}\!\!>S_2O_6\\ \begin{array}{l}NH_3-NH_3\\ NH_3-NH_3\end{array}\!\!>O\\ \begin{array}{l}NH_3\\ NH_3\end{array}\!\!>S_2O_6\end{array}\right.$$

but, according to Geuther, the formula given by Künzel must be tripled, and the salt then belongs to the dodecamin or luteocobalt series. In the absence of direct proof of the existence of luteocobalt in this salt, Künzel's formula appears the more probable of the two. The compounds above mentioned, with those which I have myself described, form the only known members of the octamin group, a further study of which will doubtless yield an ample return.

6. *Action of Ammonic Nitrite on Salts of Cobalt.* — To obtain a clear view of the nature and mode of formation of the salts of xanthocobalt, I have carefully studied the relations of ammonic nitrite to salts of cobalt under different conditions. This subject has already been examined by Erdmann,‡ and in my laboratory by Sadtler.§ Erdmann found that when a neutral solution of cobaltic chloride is mixed with a neutral solution of ammonic nitrite no turbidity ensues; but after spontaneous evaporation in the air a salt crystallizes, with the formula, as Erdmann writes it (old style): —

$$Co_2\overset{\frown}{O_3 . 2}NH_3,\ 3NO_2 + NH_4O,\ NO_2.$$

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* Blomstrand has given the same formulas with trifling variations. Chemie der Jetztzeit, p. 355.

† Gmelin-Krauts' Handbuch, vol. iii. p. 468.

‡ Journal für prakt. Chemie, xcvii. 385.

§ Am. Journal of Science and Arts [2], ix. 189.

This salt is isomorphous with the corresponding potassium salt, the crystals belonging to the rhombic system. Erdmann does not explain the reaction which takes place in the formation of this or the corresponding potassium salt, and regards the compounds in question as double salts. When slightly acid solutions were employed, Erdmann obtained, in addition to the above-mentioned salt, an ammonic salt corresponding to Fischer's salt, $Co_2(NO_2)_{12}(NH_4)_6 + 2OH_2$, as we should now write it. The existence of this salt was first remarked by Genth and myself.* Sadtler studied the action of ammonic nitrite on acid solutions of cobaltic chloride, and obtained two salts having respectively the formulas:—

$$Co_2(NO_2)_{10}(NH_4)_4 + 2OH_2,$$
$$Co_2(NO_2)_{12}(NH_4)_6 + 2OH_2,$$

but did not observe the formation of Erdmann's ammonium salt. In repeating these experiments, I always obtained Erdmann's ammonium salt, $Co_2(NH_3)_4(NO_2)_8(NH_4)_2$, in largest quantity. The crystals are uncommonly beautiful and well defined. Of these crystals,

0·3390 gr. gave 0·1783 gr. $SO_4Co = 20{\cdot}02$ per cent.

The formula requires 20·00 per cent. In one experiment, in which a little free acetic acid was present, I obtained large, dark sherry-wine colored prismatic crystals, which after solution and recrystallization gave only very thin lozenge-shaped tabular crystals, the form and appearance of which are highly characteristic. These crystals gave no reactions with salts of luteocobalt, purpureocobalt, and roseocobalt, and none with potassic chromate and dichromate, ammonic oxalate or argentic nitrate. The absence of the first-mentioned reactions shows that they do not contain $Co_2(NH_3)_4(NO_2)_8$ or $Co_2(NO_2)_{12}$, while the fact that they give no reactions with alkaline chromates and oxalates shows that they do not contain any known cobaltamin. Of these crystals,

0·1554 gr. gave 0·0974 gr. $SO_4Co = 23{\cdot}86$ per cent cobalt.
0·3081 gr. gave 0·0635 gr. $NH_3 = 20{\cdot}61$ per cent ammonia.

The formula $Co_2(NH_3)_6(NO_2)_6$ requires:—

Cobalt,	23·79	23·86
Ammonia,	20·56	20·61

These analyses are sufficient to identify the salt in question with one which Erdmann has described in the paper referred to as formed by the action of ammonia and potassic nitrite upon cobaltic chloride, unfortunately with but very scanty details. I attribute to this salt the formula

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* This Journal, 2d Series, vol. xxiv. p. 86.

$$Co_2 \left\{ \begin{array}{l} NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \\ NH_3-NO_2 \end{array} \right.$$

and consider it to be the nitrous representative of the hexamin $Co_2(NH_3)_6$. I have not succeeded in obtaining from it other members of the same series; but it is, to say the least, probable that the dichrocobalt-chloride of Fr. Rose,* $Co_2(NH_3)_6Cl_6 + 2OH_2$, represents the corresponding chloride. Künzel † has described a sulphite to which he attributes the formula

$$Co_2(NH_3)_6(SO_3)_3 + OH_2,$$

but according to Geuther ‡ this formula must be doubled, the salt belonging to the dodecamin or luteocobalt series, with the formula

$$Co_2(NH_3)_{12}(SO_3)_6 + Co_2(SO_3)_6 + 2OH_2.$$

Erdmann's hexamin salt is of special interest, because, as I shall show, it forms the first term in a remarkable series of metameric bodies: its formation under the circumstances may with great probability be expressed by the equation

$$2CoCl_2 + 10NH_4 . NO_2 + 3O = Co_2(NH_3)_6(NO_2)_6 + 4NH_4Cl + 3OH_2 + 4NO_2,$$

as the salt is not formed immediately, but only after absorption of oxygen from the air. The formation of Erdmann's ammonium salt may in like manner be represented by the equation

$$2CoCl_2 + 10NH_4 . NO_2 + 2O = Co_2(NH_3)_4(NO_2)_8(NH_4)_2 + 4NH_4Cl + 2OH_2,$$

the presence of oxygen being necessary in this case also.

In another experiment I obtained no hexamin nitrite, but only Erdmann's ammonium salt and the two salts described by Sadtler, and to which he gave respectively the formulas: —

$$Co_2(NO_2)_{10}(NH_4)_4 + 2OH_2,$$
$$Co_2(NO_2)_{12}(NH_4)_6 + 2OH_2.$$

These last salts were formed in considerable quantity mixed together as a yellow sparingly soluble crystalline powder, when a strong solution of ammonic nitrite was poured upon finely pulverized cobaltic chloride, and acetic acid was added in small excess. I consider the formation of these two salts to be represented by the equations:—

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* Untersuchungen über ammoniakalische Kobalt-Verbindungen. Heidelberg, 1871.

† Journal für prakt. Chemie, 72, p. 209. ‡ Ann. de Pharmacie, 128, p. 127.

$$2CoCl_2 + 10NH_4 . NO_2 + 3O = Co_2(NO_2)_{10}(NH_4)_4 + 6NH_3 + 3OH_2,$$
$$2CoCl_2 + 12NH_4 . NO_2 + 3O = Co_2(NO_2)_{12}(NH_4)_4 + 8NH_3 + 3OH_2.$$

Professor Sadtler has shown that in these cases also an absorption of oxygen from the air takes place. When a solution of ammonic nitrite is added to a strong alcoholic solution of cobaltic chloride, Erdmann's ammonium salt, $Co_2(NH_3)_4(NO_2)_8(NH_4)_2$, is chiefly formed, and only a small quantity of the four and six atom salts. The compound formed crystallizes from the alcoholic solution in very beautiful and well defined prismatic forms.

From the above it will be seen that at least four distinct compounds are formed by the action of ammonic nitrite upon solutions of cobaltic chloride in presence of a weak acid and of the oxygen of the air. It is at least probable that all four are formed at the same time, though in varying proportions. I have already shown that, in the presence of free ammonia and of ammonic nitrate, cobaltic chloride and ammonic nitrite yield the nitrate of the octamin series. Of the action of ammonic nitrite upon cobaltic salts in the presence of free ammonia, I shall speak in treating of the formation of the salts of xanthocobalt.

7. I have stated above that Erdmann obtained the hexamin nitrite, $Co_2(NH_3)_6(NO_2)_6$, by the joint action of potassic nitrite and ammonia upon cobaltic chloride. On repeating his experiments, I found that small quantities of this salt were formed, but that the chief products of the action were salts of xanthocobalt, the formation of which Erdmann does not appear to have noticed. Small quantities of salts of the octamin series are also formed. The filtered solution obtained in this reaction was precipitated by potassic dichromate, and the orange-red needles obtained recrystallized for analysis. Of these crystals,

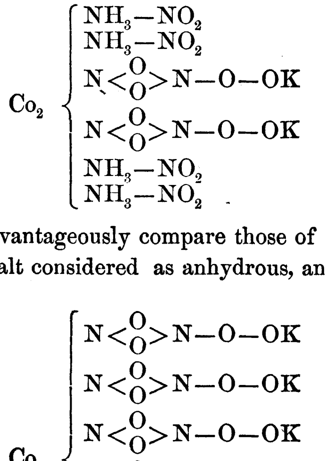
0·6145 gr. gave 0·7393 gr. $CrO_4Ba = 51{\cdot}40$ per cent Cr_2O_7.
0·7712 gr. gave 0·9277 gr. $CrO_4Ba = 51{\cdot}40$ per cent Cr_2O_7.
0·5615 gr. gave 96·5 c.c. nitrogen (moist) at 15° C. and $763{\cdot}1^{mm} =$ 20·12 per cent nitrogen.
0·5028 gr. gave 86 c.c. nitrogen (moist) at 15° C. and $763{\cdot}1^{mm} =$ 20·05 per cent nitrogen.

The formula $Co_2(NH_3)_{10}(NO_2)_2Cr_2O_7$ requires 53·22 per cent Cr_2O_7 and 20·67 per cent nitrogen, while the formula of the octamin salt, $Co_2(NH_3)_8(NO_2)_4Cr_2O_7$, requires 32·91 per cent Cr_2O_7 and 19·30 per cent nitrogen, so that the analyses leave no reasonable doubt that the salt was a mixture of a salt of xanthocobalt with a smaller proportion of the corresponding salt of the octamin series.

The above results clearly show that the action of alkaline nitrites upon salts of cobalt in presence of free acid is extremely complex, not less than six classes of salts being formed, of which two belong certainly to basic series, while three may be regarded as salts of ammonium. The sixth, $Co_2(NH_3)_6(NO_2)_6$, is probably also one term in a hexamin series.

8. The ammonia-nitrites discovered by Erdmann are of especial interest. They present the first and at present the only known instance in which cobalt, by uniting with ammonia and nitroxyl, NO_2, forms an electro-negative or chlorous radical. The compound $Co_2(NH_3)_4(NO_2)_8$ may be regarded as existing in combination with two atoms of a monatomic radical, exactly as the compound $Co_2(NH_3)_8(NO_2)_4$ combines with two atoms of chlorine. The structural formulas may be written respectively: —

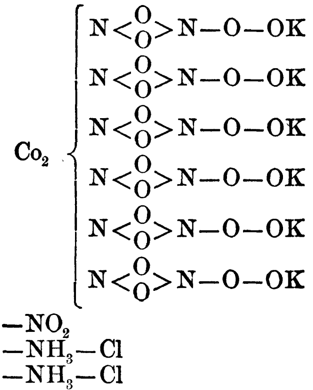
$$Co_2\left\{\begin{array}{l} NH_3-NO_2\\ NH_3-NO_2\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NO_2\\ NH_3-NO_2 \end{array}\right.$$



$$Co_2\left\{\begin{array}{l} NH_3-NO_2\\ NH_3-NO_2\\ N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK\\ NH_3-NO_2\\ NH_3-NO_2 \end{array}\right. .$$

With these formulas we may advantageously compare those of chloride of luteocobalt, of Fischer's salt considered as anhydrous, and of chloride of xanthocobalt: —

$$Co_2\left\{\begin{array}{l} NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl \end{array}\right.$$



$$Co_2\left\{\begin{array}{l} N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK\\ N<^{O}_{O}>N-O-OK \end{array}\right.$$

$$Co_2\left\{\begin{array}{l} NH_3-NO_2\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NH_3-Cl\\ NH_3-NO_2 \end{array}\right.$$

The manner in which these compounds may be derived from each other by replacement is sufficiently obvious, and is best seen by assuming chloride of luteocobalt and Fischer's salt as the two extreme terms of the series in which the other three are intermediate.

Erdmann's analyses leave no reasonable doubt as to the constitution of the ammonia-nitrites. I have thought it worth while, however, to make a few additional analyses in support of his view. In the potassium salt,

0·4497 gr. gave 0·3397 gr. SO_4Co and $SO_4K_2 = 75{\cdot}54$ per cent.
0·7338 gr. gave 0·5615 gr. „ „ $= 76{\cdot}52$ per cent.
0·5937 gr. gave 127 c.c. nitrogen at 6·5° C., and $773{\cdot}4^{mm} = 26{\cdot}45$ per cent nitrogen.

The formula $Co_2(NH_3)_4(NO_2)_8K_2$ requires 76·58 per cent ($2SO_4Co + SO_4K_2$) and 26·58 per cent nitrogen. In the silver salt,

0·3580 gr. gave 0·2902 gr. SO_4Co and SO_4Ag_2,
0·5937 gr. gave 0·1675 gr. silver $= 28{\cdot}21$ per cent.

The cobalt by difference amounts to 15·33 per cent. The formula $Co_2(NH_3)_4(NO_2)_8Ag_2$ requires 28·05 per cent silver and 15·32 per cent cobalt.

Thallium Salt. — When a solution of the potassium salt is added to one of thallous nitrate, a beautiful sherry-wine-colored crystalline precipitate is thrown down, which on recrystallization gives very well-defined prismatic crystals, having apparently the same form as the corresponding potassium and ammonium salts.

Mercurous Salt. — A solution of potassic ammonia-cobalt-nitrite gives immediately in solutions of mercurous nitrate a beautiful orange-colored crystalline precipitate, which may be dissolved in boiling water, but not without partial decomposition. The salt does not crystallize well from the solution. Of this salt,

0·7785 gr. gave 0·1775 gr. $SO_4Co = 8{\cdot}68$ per cent cobalt.

The formula $Co_2(NH_3)_4(NO_2)_8(Hg_2)_2$ requires 8·71 per cent.

A solution of the potassic salt gives no precipitate with salts of cobalt, nickel, barium, and copper, and none at first with plumbic acetate. After standing, however, a lead salt separates in fine acicular leafy crystals of a brown-orange color, soluble in hot water, but with partial decomposition. The same is true of the silver salt, but small quantities of this may usually be dissolved and recrystallized without change. The silver salt is extremely well characterized; its moderate degree of solubility and the facility with which it crystallizes in tabular lustrous crystals have made it of great service in my investigations, especially in distinguishing salts containing $Co_2(NH_3)_4(NO_2)_8$ from those which contain $Co_2(NO_2)_{12}$. Compounds of ammonia-cobalt-nitrite with barium, strontium, &c., are easily formed by double decomposition, the metallic chlorides being digested with a solution of the argentic salt. They are pale orange-yellow, soluble salts which I have not further examined. A solution of the potassic salt gives beautiful crystalline precipitates with salts of various organic alkaloids, especially with those of brucin and strychnin. These are soluble in hot water without sensible decomposition, and may be recrystallized. Salts of anilin give a bright yellow precipitate with potassic ammonia-cobalt-nitrite, which is, however, immediately decomposed, phenol being set free. The potassic salt gives also splendid crystalline precipitates with salts of croceocobalt, xanthocobalt, luteocobalt, &c. I have already noticed the salt of croceocobalt, and will describe the salts of the other bases in due course.

Erdmann has not attempted to explain the formation of this class of salts. He remarks that a yellow insoluble compound is formed at the same time with the potassic salt $Co_2(NH_3)_4(NO_2)_8K_2$, which appears to be a mixture which cannot be obtained pure for analysis. I have also obtained this body, and also regard it as consisting mainly of Fischer's salt, $Co_2(NO_2)_{12}K_6$, though, as Erdmann states, it contains a small percentage of ammonia. The formation of the salt $Co_2(NH_3)_4(NO_2)_8K_2$ may be expressed by the equation

$$2CoCl_2 + 4NH_4Cl + 8KNO_2 + O = Co_2(NH_3)_4(NO_2)_8K_2 + 6KCl + 2HCl + OH_2,$$

if we suppose oxygen to be absorbed from the air. In consequence, however, of the formation of free chlorhydric acid, N_2O_3 is set free, and it is much more probable that this is reduced by the nascent-hydrogen; so that we have

$$N_2O_3 + 2H = 2NO + OH_2.$$

The potassium salt is also formed, as I shall show, in various other cases: the similarity of some of its reactions to those of a solution of $Co_2(NO_2)_{12}Na_6$ in sodic nitrite for a long time misled me; but its relations to salts of silver, mercury, and thallium enable us to recognize its presence with absolute certainty. The salt does not enter into combination with iodine.

XANTHOCOBALT.

9. Genth and I have shown in our memoir that the salts of xanthocobalt may be formed either directly by the action of nitrous acid vapors upon salts of cobalt, or by the action of the same acid upon salts of purpureocobalt and roseocobalt, in each case in the presence of free ammonia. I propose now to give the results of a more detailed study of the subject.

With respect to the constitution of this class of salts, I may remark, in the first place, that Genth and I left it undecided whether the salts in question contain NO or NO_2, pointing out the fact that the analyses do not decide in favor of either view, and adopting the former provisionally. Braun first proved conclusively that the salts of xanthocobalt contain NO_2, and this view has since been generally adopted. I have already shown (§ 1) that when cobaltic chloride, $CoCl_2$, is mixed with ammonia and ammonic nitrite and nitrate, the solution absorbs oxygen from the air, while the nitrate of the octamin series, $Co_2(NH_3)_8(NO_2)_4(NO_3)_2$, is formed. I have not observed in this reaction the formation of a salt of xanthocobalt. If present at all, such salts must be formed in very small relative quantity. Genth and I have shown, on the other hand, that when the red gases resulting from the action of nitric acid upon starch, sawdust, or arsenous oxide are passed into solutions of cobaltic salts in presence of an excess of ammonia, salts of xanthocobalt are formed in a very short time, and in large quantity.

If we consider the red gas to consist of hyponitric oxide, N_2O_4, we may have

$$2Co(NO_3)_2 + 10NH_3 + N_2O_4 = Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4.$$

In preparing sulphate and nitrate of xanthocobalt by this process, I have on several occasions been able to detect only salts of this base among the products of the reaction. In one case, however, in which I employed cobaltic sulphate and added so large a quantity of ammonic sulphate that the solution gave no precipitate with ammonia, I obtained a very large relative quantity of Erdmann's salt $Co_2(NH_3)_6(NO_2)_6$. In other cases in which cobaltic chloride was present I detected crystals of the chloro-nitrate $Co_2(NH_8)_{10}(NO_2)_2(NO_3)_2Cl_2$. The solutions after the action of the red gases also contain small quantities of the ammonia-cobalt-nitrite of ammonium, $Co_2(NH_3)_4(NO_2)_8(NH_4)_2$, as well as ammonic nitrite and nitrate.

On the other hand, however, I have already shown (§ 3) that salts of this radical are formed in large quantity, together with a smaller proportion of the octamin nitrate, by the action of a mixture of potassic nitrite and ammonia upon cobaltic nitrate in presence of air; but that xanthocobalt is exclusively formed by the action of the same mixture upon a solution of ammonic and cobaltic sulphates. I am unable to offer any plausible explanation for the difference of the products in the two cases.

When cobaltic nitrate, ammonic nitrite, and ammonia are mixed and placed in a tightly corked bottle, no action whatever appears to take place, even after the mixture has stood some days. But if plumbic hyperoxide, PbO_2, is added, the mixture soon becomes yellow, and after a few hours large crystals of nitrate of xanthocobalt are formed, with distinct reduction of the plumbic hyperoxide. The reaction in this case may be represented by the equation: —

$$2Co(NO_3)_2 + 10NH_3 + 2NH_4 . NO_2 + PbO_2 = \\ Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 + PbO + (NH_4)_2O.$$

Potassic hypermanganate may also be employed as an oxidizing agent, but is less convenient. The experiment just detailed appears to me to render it most probable that in the action of the red gases upon salts of cobalt in presence of ammonia, the resulting salts of xanthocobalt are not formed by the direct union of the cobaltic salt with ammonia and nitroxyl, but that ammonic nitrite is first formed, and that the oxygen necessary for the completion of the reaction is derived from the decomposition of some element of the complex mixture of NO, NO_2, N_2O_3, and NO_3H, which make up the red vapors.

The formation of salts of xanthocobalt by the action of the red gas upon salts of purpureocobalt and roseocobalt in the presence of free ammonia is easily explained. We have here simple cases of double decomposition, a particular instance of which, covering in substance the whole ground, may be expressed by the equation: —

$$Co_2(NH_3)_{10}(NO_3)_6 + 2NH_4 . NO_2 = Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 + \\ 2NH_4 . NO_3.$$

Salts of xanthocobalt are always formed when salts of purpureocobalt and roseocobalt are heated or even digested in the cold with alkaline nitrites. I have made a special study of the action of potassic and sodic nitrites upon chloride of purpureocobalt, the details of which are as follows:

10. *Action of Sodic and Potassic Nitrites upon Chloride of Purpureocobalt.* — A quantity of chloride of purpureocobalt was dissolved in boiling water, with a little free acetic acid to prevent decomposition,

and added to a hot solution of potassic nitrite in excess. The dark brown-red solution was evaporated at a gentle heat to half its volume. On cooling, a small quantity of Fischer's salt, $Co_2(NO_2)_{12}K_6 + 2OH_2$, separated; afterward sherry-wine-colored prismatic crystals were formed in abundance. After recrystallization, these were analyzed.

0·2824 gr. gave 0·1519 gr. $CoSO_4 = 20·47$ per cent cobalt.
0.5557 gr. gave 0·2092 gr. silver $= 12·37$ per cent chlorine.

The same experiment was made with sodic nitrite, and with similar results. After two recrystallizations the salt formed was analyzed.

0·4163 gr. gave 0·2235 gr. $CoSO_4 = 20·43$ per cent cobalt.
0·2332 gr. gave 0·0876 gr. silver $= 12·38$ per cent chlorine.
0·6625 gr. gave 192·12 c.c. nitrogen (moist) at 14° C. and $764·1^{mm} =$ 34·29 per cent.
1·2310 gr. gave 0·5825 gr. water $= 5·24$ per cent hydrogen.
1·6542 gr. gave 0·7996 gr. water $= 5·37$ per cent hydrogen.

The salt being found to lose no water on heating, the analyses agree with the formula: —

$$Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2,$$

which requires: —

		Found.	
Cobalt,	20·52	20·47	20·43
Chlorine,	12·34	12·37	12·38
Hydrogen,	5·26	5·24	5·37
Nitrogen,	34·09	34·20	

and which is fully sustained by other considerations, as I shall show. As the solutions of the alkaline nitrites employed also contained nitrates, the formation of the new salt may be represented by the equation: —

$$Co_2(NH_3)_{10}Cl_6 + 2KNO_2 + 2KNO_3 = 4KCl + Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2.$$

The salt itself is then a nitroso-chloro-nitrate, and belongs probably to the *a*-decamin or purpureocobalt series; but it may be more conveniently regarded as the chloro-nitrate of xanthocobalt. It has the wine color of the salts of the so-called xanthocobalt series, and crystallizes usually in prismatic forms, which are moderately soluble in hot water, and separate readily from the solution. With neutral potassic chromate the salt gives the beautiful yellow crystalline chromate of xanthocobalt: —

$$Co_2(NH_3)_{10}(NO_2)_2(CrO_4)_2 + 2OH_2.$$

With potassic ferrocyanide it gives the characteristic red prismatic crystals of

$$Co_2(NH_3)_{10}(NO_2)_2FeCy_6 + 6OH_2;$$

and with ammonic oxalate, oxalate of xanthocobalt,

$$Co_2(NH_3)_{10}(NO_2)_2(C_2O_4)_2,$$

the reactions being too obvious to require explanation by equations.

As it is difficult to prevent the action of the alkaline nitrites upon chloride of purpureocobalt from going too far and decomposing the new salt first formed, I had recourse to a different mode of preparation, by which the salt can be prepared in any quantity and with the greatest facility. A hot solution containing one molecule of chloride of xanthocobalt was mixed with a solution containing one molecule of nitrate of xanthocobalt. On cooling, the chloro-nitrate crystallized in beautiful prismatic forms. In this case we have

$$Co_2(NH_3)_{10}(NO_2)_2Cl_4 + Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 = \\ 2Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2.$$

Of the crystals so formed,

0·6203 gr. gave 0·3310 gr. $CoSO_4 = 20·31$ per cent cobalt.
0·9268 gr. gave 0·3450 gr. silver = 12·24 per cent chlorine.

The formula requires 20·51 per cent cobalt and 12·34 per cent chlorine. A portion of the crystallized salt was dissolved and precipitated by argentic nitrate. The filtrate from AgCl gave on evaporation crystals of nitrate of xanthocobalt, in which

0·2972 gr. gave 0·1469 gr. $CoSO_4 = 18·81$ per cent cobalt.

The formula of the nitrate requires 18·73 per cent. These results leave no doubt as to the constitution and true relations of the chloro-nitrate.

Gold Salt. — When the chloro-nitrate is dissolved and a solution of aurochloride of sodium, $AuCl_4Na$, is added in excess, long prismatic wine-yellow crystals are formed. Of these crystals,

0·8564 gr. decomposed by zinc and sulphuric acid gave 0·6300 gr. silver = 24·16 per cent chlorine and 0·2858 gr. gold = 33·36 per cent.
0·4084 gr. gave 0·1770 gr. Au + Co = 43·34 per cent and by difference 9·98 per cent cobalt.

The formula, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2 + 2AuCl_3$, requires: —

		Found.
Cobalt	9·98	9·98
Gold	33·33	33·36
Chlorine	24·03	24.16

The salt is readily decomposed by boiling with reduction of metallic gold.

Platinum Salt. — Platinic chloride in solution precipitates the chloro-nitrate almost immediately in the form of wine-yellow needles. After recrystallization the salt was analyzed with the following results: —

0·6405 gr. fused with potassio-sodic carbonate gave 0·5564 gr. silver = 28·55 per cent chlorine, 0·1986 gr. platinum = 31·00 per cent and 0·0597 gr. cobalt = 9·33 per cent.

The platinum and cobalt were weighed together as metals after reduction by hydrogen, and the cobalt was then dissolved by long boiling with nitric acid.

The formula, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2 + 2PtCl_4$, requires: —

		Found.
Cobalt	9·40	9·33
Platinum	31·55	31·00
Chlorine	28·28	28·55

The salt lost no water on heating to 140° C.

Bromo-nitrate of Xanthocobalt. — One molecule of bromide of xanthocobalt was mixed with one of the nitrate of the same base, both salts being in solution in hot water. A dark, sherry-wine colored salt separated, after some hours, in well-defined crystals. In this salt

0·8925 gr. gave 0·4190 gr. SO_4Co = 17·86 per cent cobalt.
0·7116 gr. gave 0·1244 gr. silver = 12·94 per cent bromine.

The formula $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Br_2$ requires 17·77 per cent cobalt, and 24·09 per cent bromine. The salt was re-dissolved, and allowed to crystallize a second time. In the salt thus obtained

0·8538 gr. gave 0·3984 gr. SO_4Co = 17·76 per cent cobalt.
0·8474 gr. gave 0·2672 gr. silver = 23·62 per cent bromine.

These results leave no doubt that a definite bromo-nitrate, analogous to the chloro-nitrate, is found by direct union of the nitrate and bromide. The salt appears to be, however, much less stable than the corresponding chlorine salt. A portion of it was crystallized a third time, and then gave 23·04 per cent of bromine, indicating the commencement of a separation into bromide and nitrate. The facility with which the chloro-nitrate is formed by the direct union of its constituents, led me to attempt the formation of other new salts by a similar process. I mixed one molecule of chloride of purpureocobalt, and one of nitrate of xanthocobalt, in the hope of obtaining a salt with the formula $Co_2(NH_3)_{10}(NO_2)(NO_3)_2Cl_3$, since

$$Co_2(NH_3)_{10}Cl_6 + Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 = \\ 2Co_2(NH_3)_{10}(NO_2)(NO_3)_2Cl_3.$$

After boiling the mixture with a little free acetic acid, the solution deposited, on cooling, deep orange-red — apparently homogeneous — crystals. Of these

0·3145 gr. gave 0·1746 gr. SO_4Co = 21·13 per cent cobalt.
0·9203 gr. gave 0·5080 gr. silver = 17·99 per cent chlorine.

The formula $Co_2(NH_3)_{10}(NO_2)(NO_3)_2Cl_8$ requires 20.90 cobalt, and 18·86 per cent chlorine. The analyses seem to show that a salt having the composition given may exist. On recrystallization, the salt was more or less completely decomposed, as the following analyses show: —

0·2125 gr. gave 0·1161 gr. SO_4Co = 20·80 per cent cobalt.
0·5933 gr. gave 0·2470 gr. silver = 13·70 per cent chlorine.
0·7888 gr. gave 0·3308 gr. silver = 13·78 per cent chlorine.

These numbers approximate to those required by the formula, $Co_2(NH_3)_{10}(NO_2)_2(NO_3)_2Cl_2$. I attempted in like manner to form salts synthetically by mixing other salts in the proportions indicated by the equations: —

$$Co_2(NH_3)_{10}(NO_2)_6 + Co_2(NH_3)_{10}Cl_6 = Co_2(NH_3)_{10}(NO_2)_3Cl_3.$$

$$Co_2(NH_3)_{10}(NO_3)_6 + Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4 = \\ Co_2(NH_3)_{10}(NO_2)(NO_3)_5.$$

The experiments led, however, to no definite results.

The chloro-nitrate above described is the salt to which I, at one time, attributed the formula

$$Co_2(NH_3)_{10}(NO_2)_4Cl_2 + 2OH_2,$$

and which I regarded as the chloride of a special radical, "flavo-cobalt," $Co_2(NH_3)_{10}(NO_2)_4$. The mere analyses can hardly distinguish with certainty between the two formulas, and I was for some time misled by an erroneous interpretation of my results. The compounds of cobalt containing ammonia and nitroxyl, NO_2, have in general the same color, and differ but little in solubility, so that it is extremely difficult to separate them; and in my analyses of what I believed to be the sulphate and nitrate of the same base, I had undoubtedly to deal with impure salts of xanthocobalt. Krok* has described a salt with the formula $Co_2(NH_3)_{10}Cl(NO_2)_5 + 3OH_2$. There is no theoretical reason why such a compound should not exist, but Krok's analyses do not appear to me sufficient, as the cobalt, chlorine, and ammonia only were determined, and not the whole quantity of nitrogen in the salt. Moreover, it is not proved that the salt can be recrystallized without decomposition, or that it forms definite compounds with metallic chlorides.

As the chloride and nitrate of xanthocobalt are capable of uniting directly to form the chloro-nitrate above described, it might be supposed that the two salts are isomorphous, and, therefore, crystallize together in all proportions. According to Professor Dana's measurements, cited in the first part of this memoir, nitrate of xanthocobalt crystallizes in forms belonging to the dimetric or square prismatic system. Professor Cooke has kindly determined the form of the corresponding chloride, and finds that the crystals are either trimetric or monoclinic. The chloro-nitrate cannot, therefore, be regarded as a mixture of two isomorphous salts.

11. Finally, salts of xanthocobalt are formed by the action of Fischer's salt, $Co_2(NO_2)_{12}K_6$, upon salts of purpureocobalt and roseocobalt. When, for instance, chloride of purpureocobalt is dissolved in boiling water, with a little free acetic or chlorhydric acid, and $Co_2(NO_2)_{12}K_6$ is added, in small portions at a time, the violet color of the salt gradually disappears as the boiling continues, and the solution finally assumes a fine orange-brown tint. The filtered solution gives on cooling fine crystals of chloride of xanthocobalt, the reaction being probably expressed by the equation

$$Co_2(NO_2)_{12}K_6 + 3Co_2(NH_3)_{10}Cl_6 = 3Co_2(NH_3)_{10}(NO_2)_2Cl_4 + 6KCl + 2Co(NO_2)_2 + 2NO_2.$$

During the boiling red vapors are given off. In one experiment the chloride of xanthocobalt formed was analyzed, with the following results: —

0·5027 gr. gave 0·2987 gr. SO_4Co = 22·62 per cent cobalt.
0·7616 gr. gave 0·6351 gr. silver = 27·35 per cent chlorine.

The formula $Co_2(NH_3)_{10}(NO_2)_2Cl_4$ requires 22·52 per cent cobalt, and 27·09 per cent chlorine. The salt gave all the reactions of the chloride.

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* Acta Univers. Lund, 1870.

On the other hand, Fischer's salt is an almost constant product of the action of the alkaline nitrites upon salts of the decamin series. I have already mentioned its occurrence among the products of the action of potassic and sodic nitrite upon chloride of purpureocobalt. When nitrate of xanthocobalt is boiled with potassic nitrite and a little acetic acid, Fischer's salt is formed in abundance, and the nitrate is gradually decomposed, without formation of any other product which I could detect.

Chromate. — When neutral potassic chromate is added to a solution of nitrate of xanthocobalt, a beautiful yellow crystalline precipitate is thrown down, which may be washed with cold water, in which it is but slightly soluble. Hot water also dissolves this salt in very small quantity. The chromate has the formula

$$Co_2(NH_3)_{10}(NO_2)_2(CrO_4)_2 + 2OH_2,$$

as the following analyses show: —

0·4340 gr. gave 0·3652 gr. $CrO_4Ba = 35·96$ per cent CrO_4.
0·3472 gr. gave 0·2900 gr. $CrO_4Ba = 35·70$ per cent CrO_4.
0·6954 gr. gave 0·3370 gr. water = 5·38 per cent hydrogen.

The salt lost only 0·68 per cent water on drying up to 145° C.

The formula requires 35·84 per cent CrO_4, and 5·24 per cent hydrogen. It is remarkable that the salt should retain its water of crystallization at so high a temperature. The neutral chromate of xanthocobalt furnishes the most convenient method of obtaining the chloride and sulphate of xanthocobalt in a state of purity. For this purpose the chromate is to be boiled with water and a little acetic acid, and a solution of baric chloride added until baric chromate is no longer formed. From the filtrate the chloride of xanthocobalt crystallizes readily, and a second crystallization gives the salt perfectly pure. The sulphate may then be prepared from the chloride by double decomposition with argentic sulphate. In the preparation of the chloride by the above process, it is not necessary to operate with pure nitrate, but the crude salt and solutions obtained directly by the action of the red gases upon cobaltic nitrate and ammonia may be employed. I am even disposed to consider double decomposition of the chromate with baric nitrate the easiest method of obtaining a perfectly pure nitrate of xanthocobalt.

Dichromate. — Potassic dichromate produces in strong solutions of nitrate of xanthocobalt a beautiful orange-yellow precipitate of crystalline needles, easily purified by recrystallization, a few drops of acetic acid being added to prevent decomposition. The salt is easily soluble in hot water, and crystallizes readily, though not in well-defined crystals, from the solution. Like the neutral chromate, it is available as a means of recognizing salts of xanthocobalt, and of obtaining them in a state of purity. Of this salt

0·6570 gr. gave 0·8200 gr. $CrO_4Ba = 53·33$ per cent Cr_2O_7.
0·3974 gr. gave 0·4950 gr. $CrO_4Ba = 53·23$ per cent Cr_2O_7.
0·4868 gr. gave 0·1830 gr. $Cr_2O_3 = 53·40$ per cent Cr_2O_7.

The formula $Co_2(NH_3)_{10}(NO_2)_2(Cr_2O_7)_2$ requires 53·22 per cent.

Iodosulphates. — A solution of potassic iodide gives no precipitate at first with one of nitrate of xanthocobalt, but, after standing some time, pale brown yellow acicular crystals of the iodide $Co_2(NH_3)_{10}(NO_2)_2I_4$ are formed. When a solution of iodine in potassic iodide is added to one of nitrate of xanthocobalt, iodine is precipitated in crystals, but no hyperiodide is formed, as in the case of the iodide of the octamin series already described. Potassic iodide gives, with a solution of sulphate of xanthocobalt, brown-yellow needles, which, after re-solution, give larger prismatic crystals. Of these

0·5396 gr. gave 0·2207 gr. $SO_4Co = 15·57$ per cent cobalt.
0·8856 gr. gave 0·2689 gr. $SO_4Ba = 12·51$ per cent SO_4.
0·4541 gr. gave 0·1288 gr. silver = 33·37 per cent iodine.

The formula $Co_2(NH_3)_{10}(NO_2)_2SO_4I_2 + 2OH_2$ requires

	Calculated.	Found.
Cobalt, 2	15·40	15·57
Iodine, 2	33·16	33·37
SO_4 1	12·53	12·51

When a solution of iodine in potassic iodide is added to one of sulphate of xanthocobalt, very beautiful, deep ruby red, well-defined crystals are formed, which are readily decomposed by hot water, with evolution of iodine vapor, and cannot be recrystallized for analysis. Of these crystals

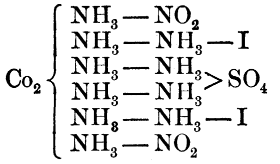
0·6094 gr. gave 86·5 c.c. nitrogen at 13° C. and $758·6^{mm}$ $(h = 2·08^{mm})$ = 16·63 per cent nitrogen.
0·2142 gr. gave 0·0687 gr. $SO_4Co = 12·21$ per cent cobalt.
0·6104 gr. gave 0·1870 gr. $SO_4Co = 11·64$ per cent cobalt.
0·3940 gr. gave 0·1672 gr. silver = 49·90 per cent iodine.
0·5437 gr. gave 0·2310 gr. silver = 49·96 per cent iodine.
0·3020 gr. gave 0·0724 gr. $SO_4Ba = 9·87$ per cent SO_4.
1·0627 gr. gave 0·2787 gr. $SO_4Ba = 10·80$ per cent SO_4.

The formula $Co_2(NH_3)_{10}(NO_2)_2SO_4I_4$ requires

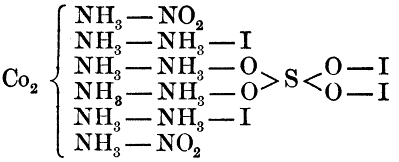
		Calculated.	Found. 1	Found. 2
Cobalt,	2	11·99	12·21	11·64
Iodine,	4	51·60	49·90	49·96
SO_4	1	9·75	9·77	10·80
Nitrogen,	12	17·07		16·63

Salts 1 and 2 were from different preparations.

The analyses do not correspond as closely to the formula as might be wished, but it must be remembered that the salt cannot be recrystallized without decomposition, and is probably not quite free from the first described, or normal iodo-sulphate. The salt gives off iodine on heating. The structural formulas of the two salts may be written as follows: —



$$Co_2\left\{\begin{array}{l} NH_3-NO_2 \\ NH_3-NH_3-I \\ NH_3-NH_3 \\ NH_3-NH_3 \end{array}\!\!>SO_4 \\ \begin{array}{l} NH_3-NH_3-I \\ NH_3-NO_2 \end{array}\right.$$



$$Co_2\left\{\begin{array}{l} NH_3-NO_2 \\ NH_3-NH_3-I \\ NH_3-NH_3-O \\ NH_3-NH_3-O \\ NH_3-NH_3-I \\ NH_3-NO_2 \end{array}\right. \quad {>}S{<}\begin{array}{l} O-I \\ O-I \end{array}$$

This mode of writing the formulas, however, involves certain theoretical conclusions, which I shall examine in detail hereafter. I added $PtCl_6Na_2$ to a solution of sulphate of xanthocobalt, hoping to obtain a salt with the formula $Co_2(NH_3)_{10}(NO_2)_2(SO_4)Cl_2(PtCl_6)$, analogous to a platinum salt of roseocobalt, which I shall hereafter describe, and which has the formula $Co_2(NH_3)_{10}(SO_4)_2PtCl_6$. The beautiful crystalline precipitate formed proved to be only the salt $Co_2(NH_3)_{10}(NO_2)_2Cl_2PtCl_6 + OH_2$, described in the first part of this memoir. 0·3882 gr. gave 0·1612 gr. $Co + Pt = 41{\cdot}52$. The formula requires 41·39 per cent.

Nitrite of Xanthocobalt. — When argentic nitrite is boiled with a solution of chloride of purpureocobalt, the liquid soon loses its fine violet color, and assumes the wine yellow tint of the salts of xanthocobalt. The filtrate from the argentic chloride gave, on careful evaporation, two distinct salts, — a salt in beautiful scaly crystals, and one in octahedral crystals. The two salts were separated by crystallization. Of the scaly salt

0·2854 gr. gave 0·2286 gr. $SO_4Co + SO_4Ag_2 = 79{\cdot}97$ per cent.

The formula of the ammonia-cobalt-nitrite, $Co_2(NH_3)_4(NO_2)_8Ag_2$ requires 80·75 per cent, and the salt was easily identified by its appearance and properties, with the silver salt of Erdmann's series. As the octahedral salt was rather difficult to obtain perfectly pure by this method, I had recourse to the decomposition of sulphate of roseocobalt by baric nitrite. A solution of the last-named salt is to be added to one of the sulphate as long as a precipitate is formed. The sherry-wine-colored filtrate is then to be cautiously evaporated, when fine dark wine-colored octahedral crystals form. Of these crystals

0·4750 gr. gave 0·2303 gr. $SO_4Co = 18·46$ per cent cobalt.
0·1220 gr. gave 0·0594 gr. $SO_4Co = 18·54$ per cent cobalt.
0·3129 gr. gave 0·0403 gr. water, when heated to 140° C. = 12·87 per cent.
0·4289 gr. gave 0·1141 gr. ammonia = 26·60 per cent.

The formula $Co_2(NH_3)_{10}(NO_2)_6 + 4OH_2$ requires

		Calculated.	Found.	
Cobalt,	2	18·55	18·46	18·54
Ammonia,	10	26·72	26·60	
Water,	4	11·32	12·87	

The percentage of water in the analysis is too high, and would seem to show that a slight decomposition of the salt had taken place. I attempted to determine the percentage of NO_2 in this salt by titrition with potassic hypermanganate, but though the analyses were made with the greatest care, I obtained as a mean of three determinations, agreeing well together, only 11·24 per cent, which would correspond to less than two atoms. In other cases also I found that the method could not be employed.

So far as the empirical formula is concerned, the salt may be regarded as a nitrite of purpureocobalt or roseocobalt, $Co_2(NH_3)_{10}(NO_2)_6 + 4OH_2$. Its solution gives, however, the reactions of salts of xanthocobalt with the greatest distinctness, and I regard it, therefore, as the normal nitrite of this series, with the formula $Co_2(NH_3)_{10}(NO_2)_2(NO_2)_4 + 4OH_2$. Its formation from sulphate of roseocobalt and baric nitrite is expressed by the equation: —

$$Co_2(NH_3)_{10}(SO_4)_3 + 3Ba(NO_2)_2 = Co_2(NH_3)_{10}(NO_2)_6 + 3SO_4Ba,$$

and from chloride of purpureocobalt and argentic nitrite, by the equation,

$$Co_2(NH_3)_{10}Cl_6 + 6AgNO_2 = Co_2(NH_3)_{10}(NO_2)_6 + 6AgCl.$$

The formation of the silver salt of Erdmann's series, $Co_2(NH_3)_4(NO_2)_8Ag_2$, is probably due to a secondary action, and may, perhaps, be expressed by the equation

$$Co_2(NH_3)_{10}(NO_2)_6 + 2AgNO_2 = Co_2(NH_3)_4(NO_2)_8Ag_2 + 6NH_3.$$

Ammonia-cobalt-nitrate of Xanthocobalt. — When a solution of potassic ammonia-cobalt nitrite is added to one of nitrate of xanthocobalt, a beautiful crystalline precipitate is formed, of a deep orange-red color, which requires a rather large quantity of boiling water for solution, and which may be recrystallized without decomposition. The solution gives the reactions of salts of xanthocobalt, and gives also, with argentic nitrate, the characteristic silver salt $Co_2(NH_3)_4(NO_2)_8Ag_2$. Of this salt

0·5074 gr. gave 0·3172 gr. $SO_4Co = 23{\cdot}77$ per cent cobalt.
0·4731 gr. gave 135 c.c. nitrogen (moist) at 12°C and $757{\cdot}8^{mm} = 33{\cdot}69$ per cent nitrogen.

The formula $\{Co_2(NH_3)_{10}(NO_2)_2\}\ \{Co_2(NH_3)_4(NO_2)_8\}_2$ requires 23·79 per cent cobalt, and 33·87 per cent nitrogen. This salt is metameric with the corresponding salt of the octamin series already described, and with Erdmann's salt, $Co_2(NH_3)_6(NO_2)_6$, since we have

$$\{Co_2(NH_3)_{10}(NO_2)_2\}\ \{Co_2(NH_3)_4(NO_2)_8\}_2 = 3Co_2(NH_3)_6(NO_2)_6.$$

In endeavoring to obtain measurable crystals by allowing a solution of this salt to stand for some time, and evaporate at ordinary temperatures, I found that the salt was partially decomposed, a considerable quantity of cobaltic nitrate being formed.

Oxalate of Xanthocobalt. — In the first part of this memoir, in consequence of an oversight, the formula given for the oxalate of xanthocobalt contains (old style) five atoms of water of crystallization. The salt is really anhydrous, and the analyses given agree with the formula $Co_2(NH_3)_{10}(NO_2)_2(C_2O_4)_2$. The salt is obtained from hot solutions in granular crystals. Its solution in hot dilute nitric acid deposits abundant crystals of the nitrate, the oxalate being almost completely decomposed. Sulphate and nitrate of xanthocobalt may be readily prepared from the oxalate by boiling with a small excess of mercurous sulphate or nitrate, adding, in the first case, a little dilute sulphuric, in the last, a little nitric, acid. As the oxalate can be precipitated by ammonic oxalate from the crude nitrate, this furnishes a cheap and expeditious method of obtaining the pure sulphate.

The formulas of the salts of xanthocobalt at present known become in the new notation: —

Chloride,	$Co_2(NH_3)_{10}(NO_2)_2Cl_4$
Bromide,	$Co_2(NH_3)_{10}(NO_2)_2Br_4$
Iodide,	$Co_2(NH_3)_{10}(NO_2)_2I_4$

Nitrate,	$Co_2(NH_3)_{10}(NO_2)_2(NO_3)_4$
Nitrite,	$Co_2(NH_3)_{10}(NO_2)_2(NO_2)_4 + 4OH_2$
Sulphate,	$Co_2(NH_3)_{10}(NO_2)_2(SO_4)_2$
Iodo-sulphate,	$Co_2(NH_8)_{10}(NO_2)_2(SO_4)I_2 + 2OH_2$
Hyperiodo-sulphate,	$Co_2(NH_3)_{10}(NO_2)_2(SO_4)I_4$
Auro-chloride,	$Co_2(NH_3)_{10}(NO_2)_2Cl_4 + 2AuCl_3 + OH_2$
Platino-chloride,	$Co_2(NH_3)_{10}(NO_2)_2Cl_4 + PtCl_4 + OH_2$
Hydrargo-chloride,	$Co_2(NH_3)_{10}(NO_2)_2Cl_4 + 4HgCl_2 + OH_2$
Oxalate,	$Co_2(NH_3)_{10}(NO_2)_2(C_2O_4)_2$
Chromate,	$Co_2(NH_3)_{10}(NO_2)_2(CrO_4)_2 + 2OH_2$
Dichromate,	$Co_2(NH_3)_{10}(NO_2)_2(Cr_2O_7)_2$
Ammonia-cobalt nitrite,	$\{Co_2(NH_3)_{10}(NO_2)_2\}\ \{Co_2(NH_3)_4(NO_2)_8\}_2$
Ferrocyanide,	$Co_2(NH_3)_{10}(NO_2)_2(FeCy_6) + 6OH_2$.

I have collected them for the purpose of convenience of reference and comparison.

PURPUREOCOBALT.

12. In the first part of this memoir Genth and I have endeavored to show that purpureocobalt and roseocobalt form two distinct series of salts; that chloride of roseocobalt, for instance, $Co_2(NH_3)_{10}Cl_6 + 2OH_2$, cannot be regarded as differing from chloride of purpureocobalt only by water of crystallization. This view has been adopted by some chemists, rejected and even ridiculed by others. I shall endeavor to show, by a more extended study and comparison of the two series of salts, that they are essentially different, and, furthermore, that, as the theory of these compounds proposed by Blomstrand suggests, there are more than two series containing the group $Co_2(NH_8)_{10}$. Reserving the discussion for the present, I proceed to the description of the salts which serve to throw light upon the question.

Auro-chloride of Purpureocobalt. — When a solution of chloro-aurate of sodium is added to a hot solution of chloride of purpureocobalt, containing a little free chlorhydric acid, no precipitate is formed at first, but after standing a few hours crystals of a new salt are deposited. The crystals in question present flat prismatic forms. They have a dark ruby-red color, with a dull violet lustre, and after standing exhibit a distinct superficial reduction of gold. Of these crystals

0·9028 gr. gave 0·3206 gr. gold, and 1·0560 gr. silver = 35·50 per cent gold, and 38·45 per cent chlorine.

0·6840 gr. gave 0·1896 gr. SO_4Co and 0·2425 gr. gold = 10·55 per cent cobalt, and 35·45 per cent gold.

		Calculated.	Found.	
Cobalt,	2	10·64	10·55	
Gold,	2	35·55	35·50	35·45
Chlorine,	12	38·44	38·45	

In the first analysis the salt was reduced by zinc and dilute sulphuric acid, the gold weighed directly, and the chlorine determined in the filtrate. In the second, the salt was heated with sulphuric acid, and the reduced gold separated from the cobaltic sulphate by dissolving the latter in boiling water. The formula of the salt is

$$Co_2(NH_3)_{10}Cl_6 + 2AuCl_3,$$

or rationally

$$\overset{vi}{Co_2}\left\{\begin{array}{l} NH_3 - Cl \\ NH_3 - NH_3 - Cl \\ NH_3 - NH_3 - Cl = \overset{v}{Au}Cl_3 \\ NH_3 - NH_3 - Cl = \overset{v}{Au}Cl_3 \\ NH_3 - NH_3 - Cl \\ NH_3 - Cl \end{array}\right.$$

From the formula it appears that the salt is unsaturated, similar salts containing four or six molecules of auric chloride being also possible.

Chloro-hydrargyrates of Purpureocobalt. — When mercuric chloride is added in excess to a solution of chloride of purpureocobalt, a rather dull red salt separates in small needles, slightly soluble in cold water, but much more easily soluble in hot water, especially in the presence of free chlorhydric acid, and readily crystallizing from the hot solution. This salt has the formula

$$Co_2(NH_3)_{10}Cl_6 + 6HgCl_2$$

as the following analyses show: —

0·5884 gr. gave 0·3922 gr. Hg_2Cl_2 = 56·60 per cent mercury.
0·4409 gr. gave 0·4025 gr. silver = 30·00 per cent chlorine

		Calculated.	Found.
Mercury,	6	56·47	56·60
Chlorine,	18	30·04	30·00

When the chloride of purpureocobalt is in excess, or when the two chlorides are mixed in the proper atomic proportions, another double salt separates in very beautiful violet-colored prismatic crystals, which, like the last-mentioned salt, are but slightly soluble in cold water, but are much more soluble in boiling water, and crystallize from the solution on cooling. This salt has the formula

$$Co_2(NH_3)_{10}Cl_6 + 4HgCl_2$$

as the following analyses show: —

0·7938 gr. gave 0·4735 gr. Hg_2Cl_2 = 50·65 per cent mercury.
0·3970 gr. gave 0·3771 gr. silver = 31·23 per cent chlorine.
0·9752 gr. gave 0·9356 gr. silver = 31·42 per cent chlorine.
1·3600 gr. gave 0·1024 gr. cobalt = 7·52 per cent cobalt.

		Calculated.	Found.
Mercury,	4	50·47	50·65
Chlorine,	14	31·35	31·23 31·42
Cobalt,	2	7·44	7·52

On Blomstrand's view the formulas of the two mercury salts may be written

$$\overset{vi}{Co_2}\left\{\begin{array}{l} NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-Cl=HgCl_2 \end{array}\right. \qquad \overset{vi}{Co_2}\left\{\begin{array}{l} NH_3-Cl \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-NH_3-Cl=HgCl_2 \\ NH_3-Cl \end{array}\right.$$

It is possible that the salt containing six atoms of mercury belongs to the roseocobalt series, as I find that it is formed when a solution of $HgCl_3Na$ is added to one of the soluble sulphate of roseocobalt, $Co_2(NH_3)_{10}(SO_4)_3+5Aq$, which I shall describe farther on. I may also remark that if the progress of science should make us acquainted with a method of determining cobalt in these salts with precision, they would enable us to determine the atomic weight of that metal with great accuracy, the first salt containing 5·54, and the second 7·44 per cent of cobalt, so that a relatively large error in the weight of $(NH_3)_{10}Hg_6Cl_{18}$, or of $(NH_3)_{10}Hg_4Cl_{14}$, would exert an inappreciable influence on the result. If we regard the salt $Co_2(NH_3)_{10}Cl_6+4HgCl_2$ as unsaturated, it ought to combine with other electro-negative chlorides to form salts with three metallic elements. I have not, however, found this to be the case, so far, at least, as the chlorides of gold and platinum are concerned.

In analyzing these salts, I found it most advantageous to determine the mercury in the form of calomel, by dissolving the salt in water, adding a little chlorhydric acid, and then reducing the mercuric to mercurous chloride by a solution of sodic hypophosphite, the solution of mercuric salt having the temperature of 40° C. The mercurous chloride was then weighed on a porous earthenware cone at 100° C. In determining chlorine it is best to dissolve the salt in hot water, with a little free sulphuric acid. The mercury may then be separated as

HgS, and the chlorine determined in the filtrate after removing the excess of SH_2 by a solution of ferric alum.

Antimonio-chloride of Purpureocobalt. — A solution of antimonious chloride added to one of chloride of purpureocobalt gives a precipitate of small, granular, dull violet-red crystals. These may be washed with strong chlorhydric acid and dried by pressure between folds of porous paper, and afterward at 100° C. Water decomposes it readily, with precipitation of SbOCl. The formula of this salt is

$$Co_2(NH_3)_{10}Cl_6 + SbCl_3,$$

as appears from the following analyses: —

0·8100 gr. gave 0·3402 gr. SO_4Co = 15·99 per cent cobalt.
0·6500 gr. gave 0·1370 gr. SbO_2 = 16·64 per cent antimony.

The formula requires 16·22 per cent cobalt, and 16·49 per cent antimony.

Bismuthous chloride gives a lilac red precipitate in solutions of chloride of purpureocobalt, insoluble in strong chlorhydric acid, and readily decomposed by water with precipitation of BiOCl.

Neutral Chromate. — When a solution of nitrate of purpureocobalt is added to one of neutral potassic chromate, a red crystalline precipitate is formed, which, after washing with cold water, may be dissolved in boiling water, with addition of a few drops of acetic acid. After some hours the neutral chromate separates in crystals, which have a peculiar red color with bronze-yellow reflections. The crystals are thin, acicular leaves. The salt dissolves rather easily in hot water, but the solution is soon more or less decomposed, unless free acid is present. The dilute solution is orange-yellow; concentrated solutions are red. The dried salt somewhat resembles litharge. Different preparations of this salt gave, on analysis, results which differed somewhat from each other, but only in the amount of water of crystallization. In one preparation

0·2637 gr. gave 0·2480 gr. CrO_4Ba = 43·17 per cent CrO_4
0·3651 gr. gave 0·0811 gr. cobalt = 22·21 per cent.
0·3598 gr. gave 0·0058 gr. water up to 170° C. = 1·61 per cent.

I consider the loss of weight on heating to arise partly from hygroscopic moisture, and partly from slight decomposition, and believe that the salt is really anhydrous. The formula

$$Co_2(NH_3)_{10}.O.(CrO_4)_2$$

requires cobalt, 21·99 per cent, and CrO_4, 43·32 per cent. The formation of the neutral chromate is expressed by the equation: —

$$Co_2(NH_3)_{10}(NO_3)_6 + 2CrO_4K_2 + OH_2 = Co_2(NH_3)_{10}.O.(CrO_4)_2 + 4KNO_3 + 2NO_3H.$$

The nitric acid set free dissolves a portion of the chromate forming the dichromate, which remains in solution. When a solution of neutral potassic tungstate, WO_4K_2, is digested with dry neutral nitrate of purpureocobalt, a pink tungstate of purpureocobalt is formed, and the liquid then gives a strong acid reaction with litmus. The reaction is probably the same as that given above for the chromate.

Potassic iodide gives a dull red crystalline precipitate with neutral chromate of purpureocobalt in solution. The analyses of this salt led to no definite formula, and the precipitate appeared to be a mixture of the chromate described, $Co_2(NH_3)_{10}.O.(CrO_4)_2$, and the iodo-chromate, $Co_2(NH_3)_{10}I_2(CrO_4)_2$. By digesting powdered chloride of purpureocobalt with neutral potassic chromate, Braun obtained a dark brown-red powder, to which he gives the formula $Co_2(NH_3)_{10}(CrO_4)_3$. According to the same writer, when powdered chloride of purpureocobalt is added, in small portions at a time, to a concentrated solution of potassic dichromate, a beautiful crystalline powder is formed, which has also the formula $Co_2(NH_3)_{10}(CrO_4)_3$. In this case chromic acid, CrO_4H_2, must be set free. When a solution of potassic chromate is added to one of chloride of purpureocobalt, the crystalline precipitate formed, according to my observations, always contains chlorine. My analyses led, however, in this case also, to no definite formula, but pointed to a mixture of the chromate $Co_2(NH_3)_{10}.O.(CrO_4)_2$, and the chloro-chromate, $Co_2(NH_3)_{10}Cl_2(CrO_4)_2$. Braun has also described a salt to which he gives the formula $2NH_3.Co_2O_3.3CrO_3 + 2NH_4Cl$, which I should write $Co_2(NH_3)_2(CrO_4)_3 + 2NH_4Cl$, but the analyses are incomplete without a determination either of ammonia or of nitrogen.

Dichromate. — A solution of potassic dichromate gives, with one of nitrate of purpureocobalt, a granular red precipitate, which may be recrystallized by solution in boiling water, to which a little acetic acid has been added. The salt then separates in small, indistinct crystals of a dark brick-red color, with bronze reflections. It is somewhat soluble in cold, and dissolves readily in boiling, water. Of this salt

0·6031 gr. gave 0·0747 gr. cobalt = 12·38 per cent.

0·7101 gr. gave 1·1252 gr. CrO_4Ba = 67·71 per cent. (Chromium = 52·2)

0·6295 gr. lost, at 105° C., 0·0077 gr. water = 1·22 per cent; at 120° C., 0·0118 gr. = 1·87 per cent; and at 133° C., 0.0166 gr. = 2·64 per cent.

At 133° C. the salt was slightly decomposed. Between 133° and 145° C. it lost 4·46 per cent with partial decomposition. These analyses correspond to the formula $Co_2(NH_3)_{10}(Cr_2O_7)_3 + OH_2$.

		Calculated.	Found.
Cobalt,	2	12·35	12·38
Cr_2O_7,	3	67·97	67·71
Water,	1	1·88	1·87

The salt was dried for two weeks *in pleno* over sulphuric acid. In preparing nitrate of purpureocobalt by Mr. Mills's process, in which an ammoniacal solution of cobaltic nitrate is oxidized by potassic dichromate, I obtained, besides the nitrate, a large quantity of beautiful orange-red crystalline scales, with gold reflections. The crystals were easily purified by recrystallization. They are readily soluble in hot water, and crystallize from the solution almost completely on cooling. The formula of this salt is $Co_2(NH_3)_{10}(Cr_2O_7)_3 + 5OH_2$, as the following analyses show: —

0·6366 gr. gave 0·0735 gr. cobalt = 11·54 per cent.

0·6447 gr. gave 0·2888 gr. CrO_3 = 63·31 per cent Cr_2O_7.

0·1740 gr. gave, up to 139° C., 0·0125 gr. water = 7·19 per cent.

0·0800 gr. gave, up to 145° C., 0·0082 gr. water = 10·25 per cent.

Mean, 8·72 per cent.

In the last water determination the salt was slightly decomposed. The formula requires

		Calculated.	Found.
Cobalt,	2	11·48	11·54
Cr_2O_7	3	63·20	63·31
Water	5	8.76	8·72 (mean.)

The difference in appearance and in the number of atoms of water in the dichromate of purpureocobalt may possibly arise from the fact that, in one case, a solution of the nitrate of purpureocobalt was poured into one of potassic dichromate in excess; in the other, the nitrate was presented to the dichromate as fast as formed, — in some sense in the nascent state. But it is singular that the two hydrates are not the same after recrystallization. A solution of potassic dichromate gives, with one of chloride of purpureocobalt, a dark red crystalline precipitate, the analyses of which pointed to a mixture of $Co_2(NH_3)_{10}(Cr_2O_7)_3$ and $Co_2(NH_3)_{10}.Cl_2(Cr_2O_7)_2$. I did not succeed in obtaining the basic dichromate $Co_2(NH_3)_{10}.O.(Cr_2O_7)_2$. In all the chromates of the cobaltamines which I have studied, the direct determination of the water of crystallization has been effected with peculiar difficulty, in consequence of the tenacity with which these salts retain water up to temperatures very near to those at which incipient decomposition occurs.

(*To be continued.*)